



High-performance flexible supercapacitor based on porous array electrodes



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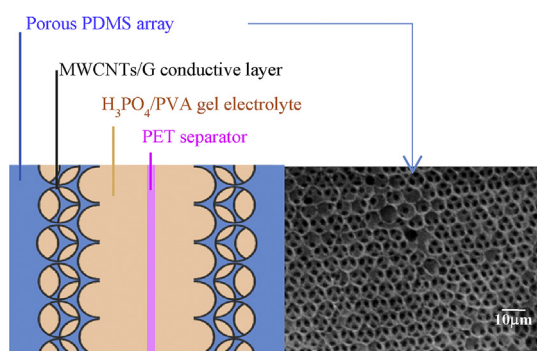
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HIGHLIGHTS

- Porous electrode was prepared using an array of polystyrene spheres as template.
- The porous electrodes provided increased contact area with the electrolyte.
- A gel electrolyte averted problems with leakage and poor interfacial contact.
- A larger separator pore size effectively reduced the internal resistance, iR_{drop} .
- Porous PDMS supercapacitor showed superior flexibility and cycling stability.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, an array of polystyrene (PS) spheres was synthesized by a dispersion-polymerization technique as a template onto which a porous polydimethylsiloxane (PDMS) microarray structure was fabricated by soft lithography. A conducting layer was coated on the surface of the microarray after a suspension of multi-walled carbon nanotubes (MWCNTs) mixed with graphene (G) had been poured into the porous array. A PDMS-based porous supercapacitor was assembled by sandwiching a separator between two porous electrodes filled with a H_3PO_4 /polyvinyl alcohol (PVA) gel electrolyte. The specific capacitance, electrochemical properties, and cycle stability of the porous electrode supercapacitors were explored. The porous PDMS-electrode-based supercapacitor exhibited high specific capacitance and good cycle stability, indicating its enormous potential for future applications in wearable and portable electronic products.

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Abbreviation: AIBN, azodiisobutyronitrile; CV, cyclic voltammetry; ED, energy density; EDLC, electric double-layer capacitor; ESEM, environmental scanning electron microscopy; G, graphene; MWCNTs, multi-walled carbon nanotubes; PANI, polyaniline; PD, power density; PDMS, polydimethylsiloxane; PET, polyethylene terephthalate; PS, polystyrene; PVA, polyvinyl alcohol; PVP, polyvinylpyrrolidone; St, styrene; SEM, scanning electron microscopy; SWCNTs, single-walled carbon nanotubes.

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1. Introduction

To satisfy the popular demand for a wide variety of portable electronics with advanced features and specifications, extensive research and development efforts have been exerted worldwide. Many recent electronic products have tended to be light, thin, and flexible, reflecting the arrival of the era of soft electronics. To

smoothly operate portable and wearable electronic products under folding, twisting, and stretching conditions, a flexible energy storage device is necessary. The successful achievement of such a device will spur the growth of soft electronics. As a corollary, the development of a flexible supercapacitor constitutes an important objective [1–4].

Supercapacitors (also known as electrochemical capacitors or electric double-layer capacitors (EDLCs)) are composed of two electrodes, an electrolyte, and a separator; they exhibit fast charge/discharge rates, long lifetimes, and high power densities. Supercapacitors are classified into EDLCs and Faradaic capacitors according to their storage mechanisms. Energy storage in EDLCs depends on the contact area between the electrode surface and the electrolyte [5,6], whereas Faradaic capacitors store charge by oxidation-reduction reactions [7]. Because of the shorter lifetimes of Faradaic capacitors, many investigators in the supercapacitor research field have focused on EDLCs [8]. Metal oxides [9,10], conducting polymers [11], and lithium ion materials [12] are typically utilized as electrode materials in EDLCs. Currently, carbon-based materials such as carbon nanotubes and graphene are also widely used as electrodes in EDLCs, recommended by their light weight, high electrical conductivity, electrochemical stability, open porosity, and other attractive features. Graphene (G) has attracted a high degree of interest for use in supercapacitors because it exhibits a very large theoretical surface area and high electrical conductivity. Nevertheless, the major problem with the use of graphene alone in a supercapacitor is that graphene sheets tend to restack, effectively reducing the available surface area, and thus, its effective capacity to store energy. To address this, adhesives have been added to prevent the conductive material from peeling off and restacking [13]. However, the added adhesives tend to reduce conductive properties, and thereby affect charge storage. The use of graphene as an electrode material *sans* adhesives for flexible energy storage is a significant objective. In other words, preparing a binder-free flexible electrode consisting of graphene sheets as a new electrode material is an important issue for the development of supercapacitors.

Another component of a supercapacitor is the electrolyte, which can be classified as one of three basic types: solid-state, liquid-state, and gel-state. Solid-state electrolytes have good mechanical properties and prevent electrolyte leakage; however, poor contact between the electrode and electrolyte can easily occur. Electrolyte leakage is a significant problem when liquid-state electrolytes are applied in flexible energy storage systems. Therefore, gel-state electrolytes are frequently used in place of the solid or liquid forms [14,15] during supercapacitor development. Using $\text{KCu}_7\text{S}_4/\text{G}$ -coated graphene paper ($\text{KCu}_7\text{S}_4/\text{G}$) as an electrode, Dai et al. [16] employed LiCl , KCl , and H_3PO_4 gels as electrolytes, and obtained energy densities of 19.0, 13.9, and 12.5 Wh/kg, respectively. According to electrochemical impedance spectroscopy (EIS) measurements, the charge transfer resistance for the $\text{KCu}_7\text{S}_4/\text{G}$ paper electrode in the H_3PO_4 electrolyte ($\sim 1.5 \Omega$) was lower than those in the KCl ($\sim 2.5 \Omega$) and LiCl ($\sim 3.2 \Omega$) electrolytes. Because low charge-transfer resistance is fairly important for the energy density of supercapacitors [17–19], we selected H_3PO_4 as the electrolyte in this study. To prepare flexible electrode substrates, metals, plastics, textiles, and sponges are the main candidate materials [2–4,20–23]. Yu et al. [24] prepared a graphene hydrogel by a hydrothermal procedure; the gel was cut into thin slices for use as an electrode. The graphene hydrogel electrode not only had high porosity and conductivity, but also possessed excellent mechanical strength, in addition to a specific capacitance of 152 F/g. In another example, polyaniline (PANI) nanowires were synthesized on graphene oxide sheets by *in situ* polymerization, and then MnO_2 was deposited on the PANI nanowires to form a $\text{PANI}/\text{MnO}_2/\text{G}$

composite. This system exhibited a specific capacitance of 695 F/g, with the device retaining $\sim 90\%$ of the initial capacitance after 1000 cycles [25]. Fan et al. [26] used a hydrothermal method involving graphene, nickel foam, and Co_3O_4 to prepare a 3-D porous structure as an electrode for a pseudo capacitor, obtaining a specific capacitance of 2459 F/g. The device retained $\sim 94\%$ of the initial capacitance after 2000 cycles. Wang et al. [27] used corncobs as electrode materials after pyrolysis/carbonization and chemical activation with KOH ; specific capacitance values of 401.6 F/g in 0.5 M H_2SO_4 and 328.4 F/g in 6 M KOH electrolyte were observed after electrochemical analysis. The high electrochemical performance of the supercapacitor was derived from the porous structure of the carbonized corncobs, which increased the surface area of the electrode and enhanced the energy storage of the device. Shieh et al. [28] prepared a uniform conductive suspension by mixing pectin and multi-walled carbon nanotubes (MWCNTs), which was then dropped onto a paper surface to form a paper-based electrode. A paper-based supercapacitor was constructed by inserting a $\text{H}_3\text{PO}_4/\text{polyvinyl alcohol}$ (PVA, $\text{MW} = 25,000$) solid-state electrolyte between two of the electrodes in a sandwich assembly, and a specific capacitance of 47 F/g was obtained. The performance measures of the aforementioned supercapacitors are listed for comparison in Table 1.

In this study, to increase the contact area between the electrode and electrolyte, the paper-based electrode was replaced by a micro-scaled porous array electrode, and H_3PO_4 and PVA were mixed as a gel electrolyte. The consequent impact on the energy storage performance of the supercapacitors was then evaluated.

2. Experimental section

2.1. Preparation and characterization of the non-close-packed polystyrene (PS) spheres template

Micro-scale PS spheres were synthesized from styrene (St) using a dispersion-polymerization method, with polyvinylpyrrolidone (PVP) as the stabilizer and azodiisobutyronitrile (AIBN) as the initiator [29]. The polymerization was carried out as follows: a mixture of ethyl alcohol (75 mL), deionized water (5 mL), St monomer (25 mL), and PVP (2.27 g) was placed in a 250 mL four-necked flask equipped with a reflux condenser and mechanical stirrer. The mixture was heated to 70 °C after it had been mixed homogeneously. Then, AIBN (0.227 g) was added and the dispersion-polymerization reaction proceeded under a nitrogen atmosphere for 24 h. After cooling, the PS spheres were separated by five centrifugal sedimentation cycles at 5000 rpm for 20 min, producing a suspension of uniformly sized PS spheres. Finally, a dilute PS suspension was prepared by mixing a portion of the PS spheres suspension (2 mL) and ethyl alcohol (10 mL) in a beaker and sonicating 10 min.

To prepare the porous array electrode, the formation of a non-close-packed array template is a crucial step. Typically, a porous array structure would be formed by pouring the polydimethylsiloxane (PDMS) prepolymer solution into the PS spheres template, curing, and removing the PS microspheres with acetone. Unfortunately, the porous array structure was not easily formed since the residual inverse structure readily collapsed once the PS microspheres were removed from the template. In this case, the PS spheres were interconnected in a typical close-packed arrangement, which limited the structural strength of the PDMS after template removal. Therefore, preparing a non-close-packed PS array template was crucial in this study. The dilute PS suspension was poured into a plasma-treated hydrophilic glass petri dish, which was rotated moving forward in a horizontal way at 30 rpm for 30 min at room temperature by a rotary shaking machine. Next,

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